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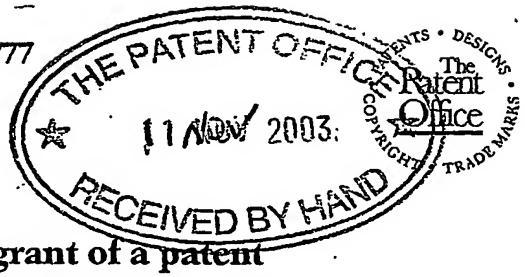

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P01/7700 0.00-0326284.7

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(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

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Cardiff Road
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1. Your reference

RC/FP6190995

2. Patent application number
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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

BASF AKTIENGESELLSCHAFT
CARL-BOSCH-STRASSE
67056 LUDWIGSHAFEN
GERMANY

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

GERMANY

6736086001

4. Title of the invention

MICROBICIDAL COMPOSITIONS AND THEIR USE

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

MEWBURN ELLIS
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Patents ADP number *(if you know it)*

109006

6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)

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Answer YES if:

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
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Microbicidal compositions and their use

Description

This invention relates to microbicidal compositions and their use.

Harmful microorganisms cause damage to many materials, productions and processes. New microbiocidal compositions for preventing this are needed, especially compositions which are effective at high pH values, i.e. at pH values above 4, and especially from 8 to 12.

Many microbiocidal compositions for combating microorganisms are commercially available. For example, microbicides known to be effective at high pH values are quaternary ammonium compounds such as cetyl pyridium chloride, di-N-decyl-dimethyl-ammonium chloride or N-hexadecyl-N,N-trimethylammonium bromide. However, these compounds generate foam and are difficult to handle. Other microbicides exist but are not stable at pH's above 10 and hence are not active, one example being the isothiazolone family.

For many years, it has been known (e.g. disclosed by DE-A 10 24 743) that metal salts, such as Ca-, Ba-, Al-, Pb-, Ag-, Cu-, Fe-, Ni-, or Zn-salts of N-alkyl-N-nitrohydroxyl-amines (also referred to as N'-hydroxy-N-alkyl diazenium oxides) are effective in inhibiting fungal growth.

DE-A 36 05 008 and DE-A 36 39 063 disclose the use of the Cu-salt of N'-hydroxy-N-cyclohexyldiazenium oxide (CuHDO) for the protection of wood.

EP-A 358 072 discloses a method of controlling organisms which grow under moist conditions, such as algae and lichen, by treatment with certain metal salts, notably copper, aluminum or tin salts, or amine salts of N'-hydroxy-N-cyclohexyldiazenium oxide. The biocidal active component may be incorporated directly into a polymer matrix, such as a polymer foil, or may be added to aqueous or organic solvent based media to be protected, such as paints, especially antifouling paints. EP-A 358 072 also discloses to use mixtures of said biocidal components together with other biocides, however, no specific examples are disclosed.

However, all of the above documents are concerned with controlling, i.e. preventing the growth of, microorganisms.

We have found surprisingly that fungi, yeast and algae can be killed by the application thereto of, specifically, the copper salt of N'-hydroxy-N-cyclohexyl-diazenium oxide (CuHDO).

We also found surprisingly that a mixture of CuHDO with any of a wide range of other biocides may exhibit an improved effect against a broad spectrum of microorganisms.

According to a first aspect, the invention provides the use, for killing fungi, yeast and algae, of a composition comprising salt CuHDO and a diluent.

According to a second aspect, the invention provides the use, for combating microorganisms of a composition comprising (A) CuHDO and (B) another additional microbicidally active component selected from a range of compounds given below. Such use may result in the killing of the microorganisms.

According to a third aspect, the invention provides a microbicidal composition comprising (A) CuHDO and (B) another additional microbicidally active component selected from a range of compounds B, given below. Application of such compositions may result in the killing of the microorganisms.

In the second and third aspects of the invention the range of compounds from which component (B) is selected is as follows:

1. Alcohols, including halogenated alcohols.
2. Isothiazolones.
3. Activated halogen compounds.
4. Formaldehyde release compounds.
5. Phenolic compounds.
6. Aldehydes.
7. Acids and esters.
8. Biphenyls.
9. Urea derivatives.
10. O-acetals, O-formals.
11. N-acetals, N-formals.
12. Benzamidines.
13. Phthalimides.
14. Pyridine derivatives.
15. Quaternary ammonium and phosphonium compounds.
16. Amines.
17. Amphoteric compounds.
18. Dithiocarbamates.
19. Compounds containing active oxygen such as peroxide.
20. Inorganic salts such as metal oxides.

Such compounds may be present, as component (B), either alone or as a mixture of any of these compounds.

Examples of alcohol compounds which may serve as the microbicidally effective component (B) are 2-bromo-2-nitropropane-1,3-diol and 2-(hydroxymethyl)-2-nitro-1,3-propanediol. Examples of isothiazolone compounds are 5-chloro-2-methyl-2H-isothiazol-3-one (CIT), 2-methyl-2H-isothiazol-3-one (MIT),1,2-benzisothiazol-3(2H)-one, 2-n-octyl-2H-isothiazol-3-one, 4,5-dichloro-2-octyl-2H-isothiazol-3-one and 2-butyl-benzo-[d]isothiazol-3-one and mixtures thereof with one another, including a mixture of CIT with MIT or mixtures of CIT or MIT with any of 1,2-benzoisothiazol-3(2H)-one, 2-octyl-2H-isothiazol-3-one, 4,5-dichloro-2-octyl-2H-isothiazol-3-one and 2-butyl-benzo[d]isothiazol-3-one. Examples of other compounds are dibromodicyanobutane, β-bromo-β-nitrostyrene, 7a-ethyldihydro-1H,3H,5H-oxazolo[3,4-c] oxazole, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(1H,3H)-dione, 1,3-dimethyl-5,5-dimethylhydantoin, diazolidinyl ureas and imidazolidinyl ureas, N'-(3,4-dichlorophenyl)-N,N-dimethyl urea, 3,3'-methylenebis(5-methyl-oxazolidine), iodo-2-propynylbutyl-carbamate, 2-sodiumsulfidopyridine-N-oxide and its metal salts, dibromonitrilopropionamide, tetrakishydroxymethylphosphonium salts, ortho-phenylphenol and salts of ortho-phenylphenol, 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane salts, (5-chloro-2,4-dichlorophenoxy)phenol, 3,4,4'-trichlorocarbanilide (triclocarban), o-benzo-p-chlorophenol, p-hydroxybenzoates, 2-(thiocyanomethylthio) benzothiazole, 3,5-dimethyl-1,3,5-thiadiazinane-2-thione, 2,4-dichlorobenzyl alcohol, chlorothalonil, methylenebis(thiocyanate), peracetic acid, 4,4-dimethyl-oxazolidine, phenoxyethanol, phenoxypropanol, 2,6-dimethyl-m-dioxan-4-ol-acetate, glutaraldehyde, glyoxal, ortho-phthalaldehyde, 4-(2-nitrobutyl)-morpholine, triazines such as 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, quaternary ammonium compounds such as benzalkoniumchloride, polyhexamethylenebiguanide salts, poly(oxyethylene(dimethyimino)ethylene(dimethylimino)-ethylene dichloride, chlorhexidine gluconate, chloroisocyanurates, halogenated hydantoins such as 1-bromo-3-chloro-5,5-dimethylhydantoin and polamines such as polyvinylamine- and polyethylene imine derivatives. Further examples include IPBC, terbutryn, ziram, zineb, dichlofluanid, trichlofuanid, folpet, metal dihexa-2,4-dienoate, tebuconazole, 3-benzo(b)thien-2-yl-5,6-dihydro-1,4,2-oxathiazine, 4-oxide, pyrithiones, thiram, cybutryne, MBT, carbendazim, diuron, chlorotoluron, fluometuron, thiabendazole, chlorothalonil, metazachlor, CuSCN, or dicopper oxide.

Preferred components (B) are 2-bromo-2-nitropropane-1,3-diol, 2-methyl-2H-isothiazol-3-one, 1,2-benzisothiazol-3(2H)-one, 2-n-octyl-2H-isothiazol-3-one, a mixture of 5-chloro-2-methyl-2H-isothiazol-3-one with 2-methyl-2H-isothiazol-3-one, dibromodicyanobutane, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(1H,3H)-dione, 3,3'-methylenebis(5-methyl-oxazolidine), 1,3-dimethyl-5,5-dimethylhydantoin, tetrakishydroxymethylphosphonium salts, ortho-phenylphenol and salts of ortho-phenylphenol, 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane salts, (5-chloro-2,4-dichlorophenoxy)phenol, 3,4,4'-trichlorocarbanilide (triclocarban), p-hydroxybenzoates, 2-(thiocyanomethylthio) benzothiazole, 3,5-dimethyl-1,3,5-thiadiazinane-2-thione, 2,4-dichlorobenzyl alcohol, chlorothalonil, methylenebis(thiocyanate),

phenoxyethanol, phenoxypropanol, triazines such as 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, quaternary ammonium compounds such as benzalkoniumchloride, polyhexamethylene biguanide salts, poly(oxyethylene(dimethyimino)ethylene (dimethylimino)ethylene dichloride, chlorhexidine gluconate, chloroisocyanurates and polyvinylamines, especially the polyamines disclosed in WO-A-97/32477.

Surprisingly it was found that CuHDO is especially suitable when applied in combination with 2-bromo-2-nitropropane-1,3-diol, 1,2-benzisothiazol-3(2H)-one, 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, 5-chloro-2-methyl-2H-isothiazol-3-one, 2-methyl-2H-isothiazol-3-one, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(2H,3H)-dione, 1,3-dimethyl-5,5-dimethylhydantoin and polyvinylamines, especially a polyamine containing from 80-100%, more preferably 90-98 wt%, vinylamine units and from 0 to 20 wt% more preferably, 2-10 wt%, vinyl formamide units.

Most preferably, the component used in combination with CuHDO is stable at high pH values.

As mentioned above, CuHDO, even as sole microbicidally active component, can be used not only to combat the growth of microorganisms, including viruses but also to kill certain microorganisms, especially fungi, more especially *Aspergillus niger* and *Chaetomium globosum*, and indeed yeasts, e.g. *Saccharomyces cerevisiae*, *Candida albicans* and *Malassezia furfur*, the yeast which causes dandruff, and certain organisms such as *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Alcaligenes faecalis*, *Staphylococcus aureus*, Staphylococcus epidermis, Corynebacterium xerosis, Propionibacterium acnes, Pityrosporum ovale, Aspergillus niger, *Alternaria alternata*, *Aspergillus versicolor*, *Aureobasidium pullulans*, *Cladosporium cladosporioides*, *Penicillium purpurogenum*, *Phoma violacea*, *Rhodotorula rubra*, *Sporobolomyces roseus*, *Stachybotrys chartarum*, *Ulocladium atrum*, *Chlorella sp*, *Pleurococcus sp*, *Nostoc muscorum*, *Oscillatoria tenuis*, *Stichococcus bacillaris*, and *Trentepohlia aurea*.

Indeed, we found surprisingly that CuHDO had a much stronger effect against fungi and algae than had been previously appreciated and is active against a broader spectrum of microorganisms, especially certain spoilage bacteria.

Accordingly, by application of CuHDO, it is thus now possible to kill, or at least control the growth of microorganisms without using toxic heavy metals such as lead or mercury.

Thus, CuHDO can be used to preserve metal working fluids, process fluids (e.g. water treatment in cooling towers or pulp and paper processing) and to protect goods such as leather, textiles, textile auxiliaries, leather auxiliaries, cosmetics, cleaners, lubricants, detergents, polymers, plastics, rubber, paper, cardboard, plastics, building materials,

cement, tiles, masonry, concrete, pigment preparations, paint formulations, adhesives and sealants against microbial attack. Preferably the CuHDO is used in industrial processes such as cooling towers and pulp and paper processing. Another preferred use of the CuHDO is the in-can preservation of formulated products such as paints and personal care products. Furthermore, as indicated above, surprisingly it was found that CuHDO is very effective in the protection of products, articles and formulations against certain spoilage bacteria, especially *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Alcaligenes faecalis* and *Staphylococcus aureus*, fungi, especially *Aspergillus niger*, *Chaetomium globosum* and *Saccharomyces cerevisiae* and especially the dandruff causing yeast *Malassezia furfur* which makes the use of CuHDO in cosmetics products, another preferred application. The microorganisms mentioned above are ubiquitous in the applications mentioned but normally hard to fight. To date, it was not known that CuHDO is effective against these difficult organisms.

CuHDO may be formulated into a concentrate based either on water or an organic solvent and optionally one or more co-formulants such as emulsifiers or pH-adjusting additives. Preferred formulations are water based and may contain low, more preferably no, volatile organic compounds (VOC). Concentrates of CuHDO may contain between 5 and 60%, more preferably between 10 and 45%, still more preferably between 20 to 40%, especially 20 to 30%, by weight of total concentrate, of CuHDO.

In application, CuHDO is preferably used so as to provide a final concentration of from 0.001 to 10%, more preferably 0.01 to 5%, especially 0.02 to 0.5%, by weight of the liquid medium (including any liquid environment to be treated).

In particular, although the pH of the CuHDO concentrate may vary from 2-12, as can that of the medium to be treated, concentrated alkaline formulations are particularly effective against microorganisms. Accordingly, it is preferred that the concentrate and more especially the treated product has a pH of at least 4, more preferably at least 7, still more preferably at least 8, especially 8 to 12.

A preferred product has a pH adjusted to at least 7, more preferably at least 8 using potassium hydroxide. In contrast with most microbicides which can be used at high pH, such as quaternary ammonium compounds, CuHDO does not generate foam and is easy to handle.

CuHDO can be formulated into e.g. pastes, emulsions or solutions or suspension or put onto solid carriers. If required surfactants, emulsifiers, chelants, solubilizers/solvents, salts, corrosion inhibitors, dyes, fragrances, anti-foaming agents or dispersants are included either alone or in combination.

As mentioned above, CuHDO, as a component (A), may be rendered even more effective by admixture with another microbicidally effective component (B), as defined above.

Compositions embodying the invention including such combinations have a particularly strong microbiocidal effect and a particularly broad spectrum and can therefore be used for combating efficiently many undesirable microorganisms. Such combined active components and formulations produced therefrom can act by a chemical route to destroy, discourage or render harmless, harmful organisms, prevent harmful effects or may act in other ways. Formulations embodying the invention may be used to prevent microbial infestation of industrial materials, in other words they can be used for in-can preservation. They serve also as microbicidal finishers of products, in other words they can be used for film conservation.

"Industrial materials" are to be understood as non-living materials, as they are attacked in technical-industrial processes. Industrial materials which can be protected from microbial damage or destruction by formulations embodying the invention are, for example, finishings, drilling oils, dispersions, emulsions, dyes, adhesives, lime, lacquers, pigment preparations, paper, paper processing materials, textiles, textile processing materials, leather, leather processing materials, wood, coating materials, anti-fouling coatings and colours, plastics articles, plastics substrates such as polyethylene, polypropylene, polyamide, polyurethane and the like, cosmetics, washing and cleaning materials, cooling lubricants, hydraulic fluids, joint sealing compounds, window cement, thickening solutions, fleeces as well as carpet layers and other materials which can be attacked or destroyed by microorganisms.

Likewise, formulations embodying the invention can be used in water treatment. Water treatment is understood as the addition of formulations to processing water, for example, combating slime in the paper industry and for control of harmful organisms in the sugar industry. They prevent or control the growth of microorganisms in cooling circulation systems, air humidification or in drilling and conveying fluid in the oil industry.

Formulations embodying the invention can be used for disinfection of, for example, bottles, instruments, hands, waste, water outflow and in washing. Here, particular examples which can be mentioned are in hospitals, nursing homes and old peoples homes, where disinfection of the above mentioned materials and objects plays a particular role, because the patients mostly have the least resistance to infection.

Microorganisms which are capable of infesting and even damaging or destroying industrial materials are bacteria, fungi (e.g. yeasts and moulds) and their spores, algae and slime organisms. Preferably the formulations embodying the invention are effective against bacteria and fungi, especially yeasts and moulds as well as algae.

Examples of gram-positive bacteria are Micrococcaceae, Streptococcaceae, Bacilli, Lactobacillaceae, Actinomycetales, especially *Mycobacterium*, *Dermatophilus*, *Nocardiaceae*, *Streptomyces* and *Corynebacterium*. Examples of gram-negative microorganisms are Spirochaetales (e.g. *Spirochaetaceae* and *Leptospiraceae*), Pseudomonadaceae, Legionellaceae, Neisseriaceae, Enterobacteriaceae, Vibrionaceae, Pasteurellaceae, Bacteroidaceae, Veillonellaceae, Rickettsiaceae, Bartonellaceae and Chlamydiaceae, as well as Brucellaceae.

Examples of yeasts include the families Cryptococcaceae and Sporobolomycetaceae in which are found human pathogenic kinds of *Candida*, *Trichospores* as well as *Cryptococcus neoformans*. Examples of these are *Candida albicans* and *Saccharomyces cerevisiae*.

An example of a mould within the family zygomycetes is Mucorales; examples of the family Hypomycetes are *Aspergillus* and *Penicillium* and an example of the family Bodariales is *Neurospora*. The representatives of moulds most mentioned are, for example, *Alternaria alternata*, *Aspergillus niger* and *Penicillium funiculosum*.

Examples of algae include Scenedesmus obliquus, Euglena gracilis, Chlorella pyrenoidosa, Chlamydomonas pulsatilla, Chlorella salina, Phaeodactylum tricornutum, Chlorella sp, *Pleurococcus sp, Nostoc muscorum, Oscillatoria tenuis, Stichococcus bacillaris and Trentepohlia aurea*.

In a composition embodying the invention comprising a combination of (A) and (B), the respective amounts of the components (A) and (B) in the composition are preferably 1 to 99 wt% of (A) and 1 to 99 wt% of (B), more preferably 10 to 90 wt% of (A) and 90 to 10% wt% of (B), especially 40 to 60 wt% of (A) and 40 to 60 wt% of (B).

As in the case of a composition containing CuHDO as sole microbicidally active component, a composition embodying the invention comprising respective components (A) and (B) may be formulated into a concentrate based either on water or an organic solvent and optionally one or more co-formulants such as emulsifiers or pH-adjusting additives. Again, preferred formulations are water based and may contain low, more preferably no, volatile organic compounds (VOC). The concentrates may contain between 5 and 60%, more preferably between 10 and 45%, still more preferably between 20 to 40%, especially 20 to 30%, by weight of total concentrate, of the combination of respective components (A) and (B).

In application, the combination of active components (A) and (B) is preferably used so as to provide a final concentration of from 0.001 to 10%, more preferably 0.01 to 5%,

especially 0.02 to 0.5%, of (A) and (B), by weight of the liquid medium (including any liquid environment to be treated).

In particular, although the pH of the concentrate may vary from 2-12, as can that of the medium to be treated, concentrated alkaline formulations are particularly effective against microorganisms. Accordingly, it is preferred that the concentrate and more especially the treated product has a pH of at least 4, more preferably at least 7, still more preferably at least 8, especially 8-12.

A preferred product has a pH adjusted to at least 7, more preferably at least 8, using potassium hydroxide.

Compositions embodying the invention comprising a combination of components (A) and (B), in dependence upon their chemical and physical properties, can be made up into the usual formulations and preparations as, for example, emulsions, suspensions, dispersions, solutions, powders, pastes or in combination with carrier materials.

To the combinations can optionally be added surface active agents such as surfactants, e.g. emulsifiers, for example, anionic surfactants such as alkylsulfonate and ethersulfate; nonionic surfactants such as fatty alcohol ethoxylate, fatty alcohol esterthiolate, sorbitan ester and polyalkylene glycol; and amphoteric surfactants; chelanats, for example, ethylenediaminetetraacetic acid, nitrilotriacetic acid and methylglycinediacetic acid; solubilizers and/or solvents, for example alcohols such as ethanol, n-propanol and i-propanol, and glycols, for example, propylene glycol and polypropylene glycol, acids and bases, for example, phosphoric acid and caustic soda, inorganic salts and/or other additives, as for example, corrosion inhibitors, anti-foaming agents, dyestuffs and fragrances, either alone or in combination with one another.

It is especially surprising that a composition embodying the invention comprising a combination of (A) CuHDO with (B) another microbicidally effective component can exhibit such a strong effect and indeed, in certain cases, an improved effect against a broad spectrum of microorganisms.

Such strong, or even improved, effects may be observed against, for example, Staphylococcus aureus, Escherichia coli, Proteus mirabilis, Citrobacter freundii, Pseudomonas fluorescens, Pseudomonas aeruginosa, Alcaligenes faecalis, Candida albicans, Saccharomyces cerevisiae, Altemaria alternata, Aspergillus niger, Penicillium funiculosum and Chaetomium globosum.

For example, a combination of (A) CuHDO and (B) Bronopol has a very strong effect against Pseudomonas aeruginosa (PSA), Candida albicans (CA), Proteus mirabilis

(PRM), Staphylococcus aureus (STA), Aspergillus niger (ASN) and Escherichia coli (EC) and exhibits a remarkable improved effect against STA, PRM, PSA and CA.

Indeed, it is particularly advantageous to use this combination against Pseudomonas aeruginosa (PSA), which is a pathogenic agent resulting in hospital infections.

Similarly, a combination of (A) CuHDO with (B) 1,2-benzisothiazol-3(2H)-one (BIT) exhibits an excellent improved effect against each of Pseudomonas aeruginosa, Staphylococcus aureus, Candida albicans and Aspergillus niger.

Embodiments of the invention will now be described in more detail with reference to the following Examples.

In can preservation

Test were performed according to the IBRG draft method (5.2, June 2001). This briefly describes the substrate being dosed with the biocide and allowed to equilibrate. Samples are inoculated once per week for 4 weeks and checked for recovery of organisms at 1,3 and 7 days after inoculation.

Results to show efficacy in a polymer based on acrylic ester and acrylonitrile at pH 9 using:

1000 ppm CuHDO
100 ppm CuHDO + 100 ppm Bronopol
100 ppm Bronopol
300 ppm Bronopol

Surface Protection

Testing was performed according to the BS3900 G6 and BBA MOAT 33 methods for evaluation versus fungi and algae, respectively. The methods involve painting a substrate panel with the coating and leaching under running water for 72 hours. The substrates are incubated for 56 days after being inoculated with fungi or algae. Performance is judged by comparing with suitable control samples ie without biocide, a positive control and for fungi with substrate panels that have not been leached.

CuHDO was evaluated against a combination product consisting in a paste of n-octyl isothiazolone, carbedazim and Diuron, as well as a reference blank.

Performance rating on painted test substrates (Score of 0,1 and 2 is considered as a pass)

0 = no growth
1 = trace of growth
2 = growth on 1-10% of test face
3 = growth on 10-30% of test face
4 = growth on 30-70% of test face
5 = growth on 70-100% of test face.

Table: Fungal resistance of coating "as applied".

TEST SAMPLE (% by weight)	FUNGAL GROWTH ASSESSMENT					
	Plaster Substrate			Wood Substrate		
	28 days	42 days	56 days	28 days	42 days	56 days
0.15% CuHDO	1	1	1	1	1	1
1.5% CuHDO	1	1	1	1	1	1
Blank Control	5	5	5	5	5	5
1.5% Combination Product	1	1	1	1	1	2

Table 2: Identification of Fungi on coatings "as applied"

TEST SAMPLE (% by weight)	FUNGAL GENERA	
	Plaster Substrate	Wood Substrate
0.15% CuHDO	none	none
1.5% CuHDO	none	none
Blank Control	*Alternaria, Cladosporium, Stachybotrys*	*Alternaria, Clasosporium, Stachybotrys*
1.5% Combination Product	none	*Alternaria*, Stachybotrys, Yeast

Table 3: Fungal resistance of coating after

TEST SAMPLE (% by weight)	FUNGAL GROWTH ASSESSMENT*					
	Plaster Substrate			Wood Substrate		
	28 days	42 days	56 days	28 days	42 days	56 days
0.15% CuHDO	1	1	2	1	1	2
1.5% CuHDO	1	1	1	1	1	1
Blank Control	3	3	4	4	4	4
1.5% Combination Product	3	3	4	3	4	5

Leached with running water for 72 hours

Table 4: Identification of Fungi on leached coatings

TEST SAMPLE (% by weight)	FUNGAL GENERA	
	Plaster Substrate	Board Substrate
0.15% CuHDO	*Stachybotrys*	*Cladosporium*, *Stachybotrys*
1.5% CuHDO	None	none
Blank Control	*Alternaria*, *Cladosporium*, *Stachybotrys*	*Alternaria*, *Cladosporium*, *Stachybotrys*, Yeast
1.5% Combination Product	*Alternaria*, *Stachybotrys*	*Alternaria*, *Stachybotrys*, Yeast

Table 5: Algal resistance of coatings after leaching

TEST SAMPLE (% by weight)	ALGAL GROWTH ASSESSMENT*		
	28 days	42 days	56 days
0.15% CuHDO	2/2	1/1	0/1
1.5% CuHDO	0/0	0/0	0/0
Blank Control	4/4	4/4	4/5
1.5% Combination Product	0/0	0/1	0/1

Leached with running water for 72 hours

Table 6: identification of algae on leached

TEST SAMPLE (% by weight)	ALGAL SPECIES
0.15% CuHDO	*Trentepohlia aurea*
1.5% CuHDO	none
Blank Control	Mixed algal species, as inoculum
1.5% Combination Product	*Trentepohlia aurea*

Claims

1. Use, for killing fungi, yeast, and algae, of a composition comprising a copper salt of N'-hydroxy-N-cyclohexyldiazenium oxide (CuHDO) and a diluent.

2. Use according to claim 1, wherein the CuHDO is the sole active component of the composition.

3. Use according to claim 1, wherein the composition additionally comprises another microbicidally active component selected from: alcohols, isothiazolones, activated halogen compounds, formaldehyde release compounds, phenolic compounds, aldehydes, acids and esters, biphenyls, urea derivatives, O-acetals, O-formals, N-acetals, N-formals, benzamidines, phthalimides, pyridine derivatives, quaternary ammonium and phosphonium compounds, amines, amphoteric compounds, dithiocarbamates, compounds containing active oxygen and mixtures of any of these.

4. Use according to claim 3, wherein the other active component is selected from at least one of 2-bromo-2-nitropropane-1,3-diol, 1,2-benzisothiazol-3(2H)-one, 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, 5-chloro-2-methyl-2H-isothiazol-3-one, 2-methyl-2H-isothiazol-3-one, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(2H,3H)-dione, 1,3-dimethyl-5,5-dimethylhydantoin and a polyvinylamine.

5. A method of killing, fungi, yeast and algae, which method comprises administering to the fungi a composition comprising a copper salt of N'-hydroxy-N-cyclohexyldiazenium oxide (CuHDO) and a diluent.

6. A method according to claim 5, wherein the CuHDO is the sole active component of the composition.

7. A method according to claim 6, wherein the composition additionally comprises another microbicidally active component selected from: alcohols, isothiazolones, activated halogen compounds, formaldehyde release compounds, phenolic compounds, aldehydes, acids and esters, biphenyls, urea derivatives, O-acetals, O-formals, N-acetals, N-formals, benzamidines, phthalimides, pyridine derivatives, quaternary ammonium and phosphonium compounds, amines, amphoteric compounds, dithiocarbamates, compounds containing active oxygen and mixtures of any of these.

8. A method according to claim 7, wherein the other active component is selected from at least one of 2-bromo-2-nitropropane-1,3-diol, 1,2-benzisothiazol-3(2H)-

one, 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, 5-chloro-2-methyl-2H-isothiazol-3-one, 2-methyl-2H-isothiazol-3-one, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(2H,3H)-dione, 1,3-dimethyl-5,5-dimethylhydantoin and a polyvinylamine.

9. Use, for combating microorganisms, of a composition comprising (A) a copper salt of N'-hydroxy-N-cyclohexyldiazenium oxide (CuHDO) and (B) another additional microbicidally active component selected from: alcohols, isothiazolones, activated halogen compounds, formaldehyde release compounds, phenolic compounds, aldehydes, acids and esters, biphenyls, urea derivatives, O-acetals, O-formals, N-acetals, N-formals, benzamidines, phthalimides, pyridine derivatives, quaternary ammonium and phosphonium compounds, amines, amphoteric compounds, dithiocarbamates, compounds containing active oxygen and mixtures of any of these.

10. Use according to claim 9, wherein the active component (B) is selected from at least one of 2-bromo-2-nitropropane-1,3-diol, 1,2-benzisothiazol-3(2H)-one, 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, 5-chloro-2-methyl-2H-isothiazol-3-one, 2-methyl-2H-isothiazol-3-one, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(2H,3H)-dione, 1,3-dimethyl-5,5-dimethylhydantoin and a polyvinylamine.

11. Use according to claim 9 or claim 10, whereby the microorganisms are either killed, or inhibited or controlled.

12. A method of combating microorganisms, which method comprises administering to the microorganisms a composition comprising (A) a copper salt of N'-hydroxy-N-cyclohexyldiazenium oxide (CuHDO) and (B) another additional microbicidally active component selected from: alcohols, isothiazolones, activated halogen compounds, formaldehyde release compounds, phenolic compounds, aldehydes, acids and esters, biphenyls, urea derivatives, O-acetals, O-formals, N-acetals, N-formals, benzamidines, phthalimides, pyridine derivatives, quaternary ammonium and phosphonium compounds, amines, amphoteric compounds, dithiocarbamates, compounds containing active oxygen and mixtures of any of these.

13. A method according to claim 12, wherein the active component (B) is selected from at least one of 2-bromo-2-nitropropane-1,3-diol, 1,2-benzisothiazol-3(2H)-one, 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, 5-chloro-2-methyl-2H-isothiazol-3-one, 2-methyl-2H-isothiazol-3-one, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(2H,3H)-dione, 1,3-dimethyl-5,5-dimethylhydantoin and a polyvinylamine.

14. A method according to claim 12 or claim 13, wherein the microorganisms are either killed or inhibited or controlled.

15. A microbicidal composition comprising (A) a copper salt of N'-hydroxy-N-cyclohexyldiazenium oxide (CuHDO) and (B) another additional microbicidally active component selected from: alcohols, isothiazolones, activated halogen compounds, formaldehyde release compounds, phenolic compounds, aldehydes, acids and esters, biphenyls, urea derivatives, O-acetals, O-formals, N-acetals, N-formals, benzamidines, phthalimides, pyridine derivatives, quaternary ammonium and phosphonium compounds, amines, amphoteric compounds, dithiocarbamates, compounds containing active oxygen and mixtures of any of these.

16. A composition according to claim 15, wherein the active component (B) is selected from at least one of 2-bromo-2-nitropropane-1,3-diol, 1,2-benzisothiazol-3(2H)-one, 1,3,5-tris-(2-hydroxyethyl)-1,3,5-hexahydrotriazine, 5-chloro-2-methyl-2H-isothiazol-3-one, 2-methyl-2H-isothiazol-3-one, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)-imidazo[4,5-d]imidazole-2,5(2H,3H)-dione, 1,3-dimethyl-5,5-dimethylhydantoin and a polyvinylamine.

17. A composition according to claim 15 or claim 16, wherein the respective amounts of the components (A) and (B) in the composition, by weight of the total amount of (A) and (B), are (A) 1 to 99 wt% and (B) 1 to 99 wt%.

18. A composition according to claim 15, wherein the said respective amounts of (A) and (B) are (A) 40 to 60 wt% and (B) 40 to 60 wt%.

19. A composition according to any one of claims 15 to 18, in the form of a paste, emulsion or solution or suspension.

20. A composition according to claim 19, having a pH of at least 4.

21. A composition according to claim 20, having a pH of at least 7.

22. A composition according to claim 21, having a pH of from 8 to 12.

Microbicidal compositions and their use

Abstract

A composition comprising a copper salt of N'-hydroxy-N-cyclohexyldiazenium oxide (CuHDO) and a diluent is useful for killing, fungi, algae, and yeasts. Such a composition but which additionally includes at least one of certain other biocidal active components is useful for combating microorganisms in general. Such other active component is selected from: alcohols, isothiazolones, activated halogen compounds, formaldehyde release compounds, phenolic compounds, aldehydes, acids and esters, biphenyls, urea derivatives, O-acetals, O-formals, N-acetals, N-formals, benzamidines, phthalimides, pyridine derivatives, quaternary ammonium and phosphonium compounds, amines, amphoteric compounds, dithiocarbamates, compounds containing active oxygen and mixtures of any of these.

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